Remediation of PAH-contaminated soils by magnetite catalyzed Fenton-like oxidation

M. Usman [a,b], P. Faure [b], C. Ruby [a], K. Hanna [c,d,*]

[a] Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, LCPME, UMR 7564 CNRS-Université de Lorraine, 405 rue de Vandoeuvre, 54600, Villers Les Nancy, France
[b] Géologie et Gestion des Ressources minérales et énergétiques, G2R, UMR 7566, CNRS-Université de Lorraine, 54506, Vandoeuvre Les Nancy, France
[c] Ecole Nationale Supérieure de Chimie de Rennes, UMR CNRS 6226 "Sciences Chimiques de Rennes", Avenue du Général Leclerc, 35708 Rennes Cedex 7, France
[d] Université Européenne de Bretagne, France

ABSTRACT

This is the premier study reporting the degradation of polycyclic aromatic hydrocarbons (PAHs) through Fenton-like oxidation catalyzed by magnetite. Kinetic degradation of PAHs was studied at circumneutral pH by treatments: (i) H_2O_2 + soluble Fe^{II} (F), (ii) H_2O_2 + magnetite as iron source (FL) and (iii) H_2O_2 alone without catalyst (HP). Results show that oxidation of a model PAH compound (fluorenone) spiked on sand resulted in its complete removal by FL treatment but degradation did not exceed 20% in HP or F systems. However, in two PAHs polluted soils (sampled from coking plant sites), negligible oxidation of 16 PAHs was observed regardless of the catalyst used: soluble Fe^{II} or magnetite. Then organic extract separated from these soils was added to sand and after evaporation of the solvent, oxidation was performed which resulted in more than 90% of PAHs removal by FL as compared to 15% by F or HP systems. These removal extents decreased by a factor of two when the organic extracts were oxidized in the presence of original soil. PAHs degradation extent was improved in soils pre-treated with availability-enhancement agents such as ethanol or cyclodextrin. Degradation was non-selective and no by-products were observed by GC–MS and μFTIR. Treatment efficiency was highly limited by PAHs availability in soils and the soil matrix effect. This study points out the promising efficiency of magnetite for PAHs oxidation at circumneutral pH over soluble Fe^{II} in contaminated soils, and has important implications in the remediation of contaminated soils.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are toxic organic contaminants of great environmental and health concern, which consist of two or more fused aromatic rings. The 16 PAHs in the US EPA list are considered as priority pollutants by US EPA and European community. Soil matrices contaminated with PAHs abound at the sites of coke-oven gas plants, refineries, and many other major chemical industries. Owing to the persistence of PAHs in soil and sediments and their toxic, mutagenic, and carcinogenic effects, the remediation of PAH-contaminated sites is an important environmental issue. Different remediation techniques have been explored for the removal of persistent PAHs from complex matrices like soils or sediments. In situ chemical oxidation (ISCO) has emerged as a cost-effective and viable remediation technology for the treatment of several pollutants in ground waters, soils and sediments. The most common oxidants used in ISCO techniques are permanganate, persulfate and H_2O_2 combining with iron (Fenton's reagent) [1]. Fenton treatments are showing great potential to oxidize PAHs in contaminated soils [2–5]. Fenton treatments utilize the high reactivity of hydroxyl radical (•OH), a powerful oxidant that attacks organic pollutants generating smaller molecules [6].

The Fenton's process is limited by the optimum pH (~3) required to inhibit the Fe^{II} precipitation and by the production of large amounts of ferric hydroxide sludge. In soil systems, such low pH in conventional Fenton reaction results in negative impacts on soil properties and quality and is incompatible with subsequent re-vegetation or biodegradation [7,8]. This low pH can be avoided by using iron minerals or chelating agents [2,5]. But chelating agents can act as hydroxyl radical scavenger [9], thereby reducing the oxidation efficiency. Hence, Fenton-like oxidation is developed to extend its range of applicability to native soil circumneutral pH. In Fenton-like oxidation, iron minerals are used instead of soluble iron to produce hydroxyl radical for an efficient degradation of organic contaminants at circumneutral pH [5,10–12].

* Corresponding author at: Ecole Nationale Supérieure de Chimie de Rennes, UMR CNRS 6226 "Sciences Chimiques de Rennes", Avenue du Général Leclerc, 35708 Rennes Cedex 7, France. Tel.: +33 2 23 23 80 27; fax: +33 2 23 23 81 20.
E-mail address: khalil.hanna@ensc-rennes.fr (K. Hanna).

The degradation of PAHs has been reported by Fenton-like reaction catalyzed by various Fe^{III} oxides like ferrihydrite, hematite or goethite [3,5,12] but all these investigations were based on spiked or artificially contaminated soils. Recently, Fe^{II}-bearing minerals like magnetite (Fe_3O_4) were found to be the most effective catalyst as compared to the only Fe^{III} oxides for heterogeneous catalytic oxidation of organic pollutants [11,13–15]. To date, the reactivity of magnetite has not been explored in heterogeneous catalysis of PAHs chemical oxidation. This is the first study investigating the removal of PAHs from two different contaminated soils through Fenton-like oxidation catalyzed by magnetite. To attain this goal, batch experiments were conducted to evaluate the ability of magnetite to catalyze Fenton-like oxidation at circumneutral pH. For comparison purpose, PAHs degradation was also investigated by using H_2O_2 catalyzed by soluble Fe^{II} and H_2O_2 alone without iron activation at circumneutral pH. Kinetic degradation of PAHs was studied over a period of 1 week. In first part of the study, oxidation of fluorenone (used as model compound) was investigated. Then the ability of magnetite or soluble Fe^{II} was tested to catalyze H_2O_2 decomposition for the degradation of PAHs found in two former coking plant soils. These soils are located in the Northeast of France. The limiting factors such as soil matrix effect or PAHs availability were addressed by conducting oxidation experiments on (i) soil organic extracts spiked on sand and (ii) soils pretreated using extracting agents (chloroform, ethanol or cyclodextrin). The oxidation was studied versus time and organic analyses were performed by GC–MS and μFTIR.

2. Experimental

2.1. Chemicals

Pure fluorenone 98%, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were purchased from Sigma–Aldrich Co. Hydroxypropyl-β-cyclodextrin (HPCD) was supplied by Sigma–Aldrich and used without further purification. Hydrogen peroxide 35% (H_2O_2) was obtained from Acros Organics. Ethanol was used as provided by Carlo Erba. Dichloromethane and chloroform were purchased from VWR and used as received. Deionized water was produced with a Milli-Q system from Millipore.

Magnetite used in this study was synthesized and characterized by X-ray powder diffraction and Mössbauer spectroscopy. Synthesis procedure and characterization of the magnetite ($Fe^{II}Fe_2^{III}O_4$) are summarized in the supporting information (Fig. S1). Fontainebleau sand, with a grain size range of 150–300 μm (mean diameter 257 μm) obtained from Prolabo was used as a support for the oxidation experiments. The sand was cleaned with 1 M HCl to remove metal impurities. Rinsing with oxygenated water was done to remove organic matter. The mineralogy of the sand was characterized by X-ray diffraction and was found to be exclusively quartz.

2.2. Soil samples

The study concerns the contaminated soils of two former coking plant sites (Homécourt (H) and Neuves-Maisons (NM)) that were located in the Northeast of France. The properties of both soils are summarized in Table 1 and were previously detailed [16]. Both soils are dominated by sand mineral fractions (more than 60%), and are almost similar in the initial PAH contamination and mineral size fraction distributions. As shown in Table 1, the total Fe content was also similar in both soils. However, the pH differs from neutral (NM) to basic (H) that could be related to 10 times higher carbonate contents in H than NM soil. Extractable organic matter (EOM)

Table 1
Physico-chemical parameters and total elemental analyses of soil samples.

	H soil	NM soil
Clay (<2 μm) (g kg^{-1})	99	126
Fine silt (2–20 μm) (g kg^{-1})	151	164
Coarse silt (20–50 μm) (g kg^{-1})	91	97
Fine sand (50–200 μm) (g kg^{-1})	184	120
Coarse sand (200–2000 μm) (g kg^{-1})	475	493
Agronomic parameters		
pH (water)	8.35	7.20
Total CaCO$_3$ (g kg^{-1})	369	38
Phosphorus P$_2$O$_5$ (g kg^{-1})	0.090	0.287
Total organic carbon (g kg^{-1})	102.0	70.6
Total nitrogen (g kg^{-1})	2.25	2.70
C/N	45.4	25.8
Solvent extractable organic matter (g kg^{-1})	36.81	13.37
16 PAHs (mg kg^{-1})	1369	1279
Total elemental analysis (%)		
Al$_2$O$_3$	6.78 ± 0.03	7.58 ± 0.40
CaO	13.92 ± 0.49	12.58 ± 0.68
Fe$_2$O$_3$	24.34 ± 0.76	24.44 ± 0.38
MgO	1.76 ± 0.06	1.71 ± 0.13
MnO	0.34 ± 0.00	0.93 ± 0.15
P$_2$O$_5$	0.65 ± 0.03	0.77 ± 0.03
SiO$_2$	17.76 ± 0.84	25.66 ± 0.78
K$_2$O	0.53 ± 0.07	1.37 ± 0.16
Na$_2$O	0.14 ± 0.08	0.50 ± 0.10
Loss by combustion	29.23 ± 0.68	24.04 ± 1.70
Total	95.46	99.58

contents were also higher in H than NM. The major element concentrations were approximately the same in both soils. NM soil sample contained significant contents of Zn (~2500 mg kg^{-1}) and Pb (~580 mg kg^{-1}) that were, respectively, 10 and 4 times higher than in the H soil sample [16].

Soil samples were crushed to 500 μm. Oxidation was performed on the dried soil samples. Organic extracts of both soils were isolated through automatic extractor Dionex® ASE 200 (Accelerated Solvent Extractor) at 100 °C and 130 bar with dichloromethane (DCM). Soil organic extract is composed of EOM which is isolated by organic solvent extraction from soil (mineral fractions and insoluble organic matter (IOM)). IOM is not soluble in organic solvent and thus, could not be extracted by solvent.

2.3. Oxidation procedures

The oxidation experiments with H_2O_2 were investigated in the following different systems: (1) model pollutant, fluorenone spiked on sand, (2) H and NM soil samples, (3) organic extracts of H and NM soils that were spiked on sand, (4) H and NM organic extracts with soil and (5) H and NM soil pretreated with addition of availability-enhancement agents.

For the first and third systems, quartz sand was served as a support matrix for the oxidation experiments. A solution of fluorenone was added into sand to have 4 mg of fluorenone per gram of sand. In third system, organic extracts isolated from soils were mixed with sand. The DCM was removed by evaporation under continuous mixing to ensure homogeneous contaminant distribution.

In contrast to the second system where the soil was subjected to oxidation without any preliminary treatment, the soil has undergone different chemical pretreatment before oxidation in the latter two systems. For the forth system, soil samples were agitated in chloroform during 45 min at 60 °C. Normally, this method is used for organic extraction of soils. But here, organic extract was not withdrawn from the system; instead it was evaporated to dryness. Our purpose here was to increase PAHs availability as it can be achieved by soil extraction. In last system, ethanol and cyclodextrin were used as solubility enhancement agents of PAHs in soils. Pure ethanol (99%) was added (5 mL/g) and next day, it was removed by

evaporation. Cyclodextrin solution (10 mM) was mixed with soil overnight prior to oxidation.

All the oxidation experiments were conducted at circumneutral pH with (i) H_2O_2 alone without catalyst (HP), (ii) H_2O_2 + soluble Fe^{II} (F) and H_2O_2 + magnetite (10%, w/w) (FL). In order to compare activation ability of both catalysts, an equivalent molar amount of Fe was used. Oxidant dose was used according to H_2O_2:Fe molar ratio of 10:1 and 20:1 for fluorenone and PAHs degradation, respectively (Table 2). A molar ratio of 10:1 for H_2O_2/Fe was employed for fluorenone oxidation according to our previous findings [9,15]. Higher amount of oxidant (20:1 for H_2O_2/Fe) was used for the oxidation of PAHs because of natural oxidant demand induced by the presence of organic and mineral constituents along with PAHs in soils (Table 1). Blank experiments were carried out with magnetite alone under the same conditions except no oxidant was added, to study possible desorption or degradation of the pollutants (Table 2).

Batch series were prepared by assigning one batch for each time point (1 h, 6 h, 24 h, 48 h and 1 week) to study the kinetic degradation of PAHs. All batch experiments were performed in triplicates. All results were expressed as a mean value of the 3 experiments and standard deviation of the three replicates was less than 5%. All experimental runs were performed at room temperature and in the absence of light obtained by aluminum foil coverings to avoid any photolytic degradation. In the standard procedure, soil slurries were prepared by adding water and catalysts (magnetite or soluble Fe^{II}) to solid matrix (2 g). The amount of water to be added was determined in order to have a final solution volume (including the oxidant volume to be added) of 20 mL. The pH was initially adjusted at 6.8 ± 0.2 for fluorenone and organic extract isolated form soil and then checked during the whole course of oxidation. In the presence of soil, oxidation experiments were performed without pH adjustment. After stirring the suspension for 15 min, the H_2O_2 oxidant was slowly added. At a specified reaction time, the corresponding batch was withdrawn from the series and was frozen to stop reaction. The samples were then freeze dried to remove water.

2.4. Instrumental analysis

The freeze dried samples were extracted in chloroform during 45 min at 60 °C. The volume was reduced to 20 mL under nitrogen flow and 5 mL of the solution was dried and weighed to determine the residual amount of EOM.

GC–MS quantification of reactant and products were performed by adding internal standards to the samples. An internal deuterated PAHs standard mix (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, supplied by Cluzeau) was added. A 2 μL amount of solution was then injected into an Agilent Technologies 6890 gas chromatograph equipped with a DB 5-MS (length: 60 m; diameter: 0.125 mm) capillary column coupled to an Agilent Technologies 5973 mass spectrometer operating in full scan mode. The temperature program was the following: 60–250 °C at 15 °C min^{-1}, then 250–315 °C at 3 °C min^{-1}, and 60 min holds at 315 °C. The carrier gas was helium at 1.5 mL min^{-1} constant flow.

The micro Fourier transform infrared (μFTIR) spectroscopic analysis were performed on an infrared spectrometer Bruker IFS55 coupled with a Multipurpose Bruker IR microscope equipped with a MCT detector cooled with liquid N_2. EOM were analyzed as described by Faure et al. [17] using a diamond window in order to avoid drawbacks usually encountered when using bulk infrared on KBr pellets, such as contamination by water adsorbed on the highly hygroscopic KBr [18]. The spectra were recorded with the following conditions: size of the analyzed area 60 μm^2, 64 accumulations (32 s), spectral resolution 4 cm^{-1}, gain 4.
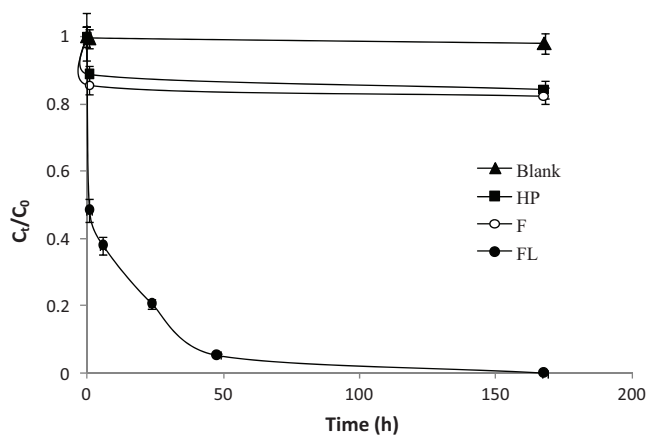

Fig. 1. Degradation of fluorenone (spiked on sand) during oxidation experiments by: H_2O_2 alone without iron activation (■ – HP), H_2O_2 + soluble Fe^{II} (○ – F) and H_2O_2 + magnetite (● – FL). Blank (▲) experiment was performed in the presence of magnetite but without any oxidant. This degradation is represented in terms of C_t/C_0 where C_t is the fluorenone concentration at specified oxidation time and C_0 is the concentration at $t = 0$ (before oxidation) measured by GC–MS. Lines are only visual guide. Experimental conditions were: solid matrix = 2 g, volume of solution = 20 mL. Oxidant dose was used according to H_2O_2:Fe molar ratio of 10:1.
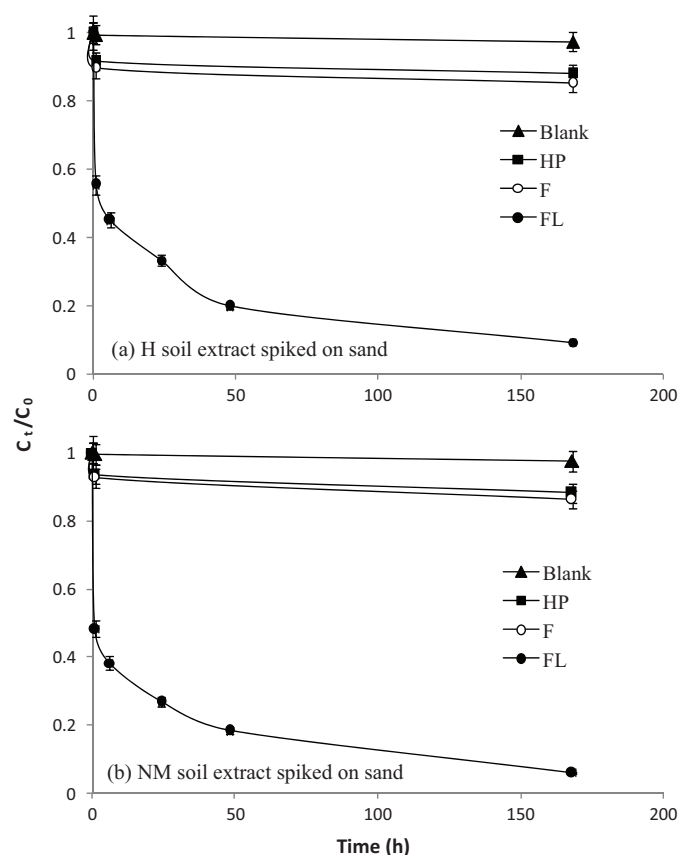

Fig. 2. PAHs degradation in H and NM organic extracts (spiked on sand) during oxidation experiments by: H_2O_2 alone without iron activation (■ – HP), H_2O_2 + soluble Fe^{II} (○ – F) and H_2O_2 + magnetite (● – FL). Blank (▲) experiment was performed in the presence of magnetite but without any oxidant. This degradation is represented in terms of C_t/C_0 where C_t is the sum of 16 PAHs concentration at specified oxidation time and C_0 is their concentration at $t = 0$ (before oxidation) measured by GC–MS. Lines are only visual guide. Experimental conditions were: solid matrix = 2 g, volume of solution = 20 mL. Oxidant dose was used according to H_2O_2:Fe molar ratio of 20:1.

Table 2
Batch slurry oxidation tests where FL: H_2O_2 + magnetite, F: H_2O_2 + soluble Fe^{II} and HP: H_2O_2 alone without iron activation. Blank experiments were performed in the presence of magnetite but without any oxidant.

Samples[a]	Test	Catalyst type[b]	Oxidant dose (H_2O_2/Fe)
(1) Fluorenone spiked on quartz sand	FL	Magnetite	10
	F	Soluble Fe^{II}	10
	HP	No iron catalyst	Same oxidant dose as for F and FL[c]
	Blank	Magnetite	No oxidant
(2) H and NM soils	FL	Magnetite	20
	F	Soluble Fe^{II}	20
	HP	No iron catalyst	Same oxidant dose as for F and FL[c]
	Blank	Magnetite	No oxidant
(3) H and NM soil organic extracts spiked on quartz sand	FL	Magnetite	20
	F	Soluble Fe^{II}	20
	HP	No iron catalyst	Same oxidant dose as for F and FL[c]
	Blank	Magnetite	No oxidant
(4) H and NM soils in pretreated soils	FL	Magnetite	20
	F	Soluble Fe^{II}	20
	HP	No iron catalyst	Same oxidant dose as for F and FL[c]
	Blank	Magnetite	No oxidant

[a] Detailed description of initial samples is given in Section 2.
[b] Magnetite was mixed with solid matrix in a ratio of 10% (w/w). An equivalent molar amount of Fe was used to compare the catalytic activity of soluble Fe^{II} and magnetite.
[c] As no iron was used here so the same oxidant dose was applied as for F and FL treatments.

3. Results and discussion

3.1. Degradation of fluorenone

Firstly the degradation of fluorenone was studied by applying H_2O_2 alone without a catalyst (HP) or H_2O_2 catalyzed by soluble Fe^{II} (F) or magnetite (FL). The pH was checked along the experiment and stayed almost constant (6.8 ± 0.2). The fluorenone was chosen as model pollutant due to its higher solubility, mobility and abundance in PAHs-contaminated soils [19]. Abatement of fluorenone was monitored by EOM evolution and GC–MS quantification, both of which are in agreement. The recovered EOM from
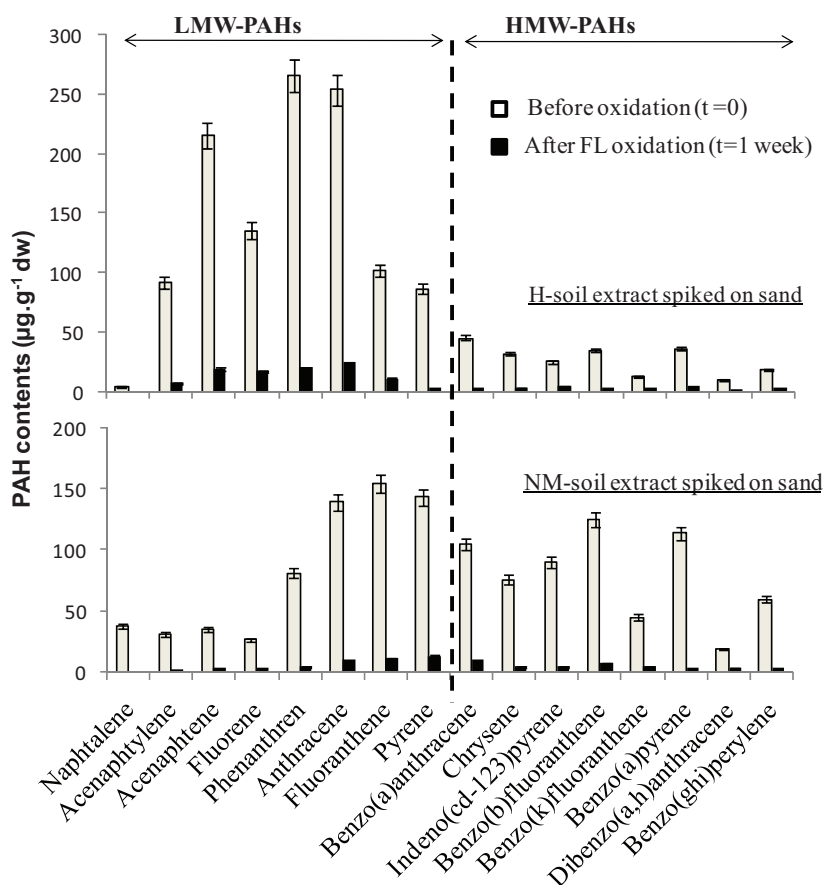

Fig. 3. Contents of individual PAHs in H and NM organic extracts (spiked on sand) at $t = 0$ before oxidation (□) and after 1 week FL oxidation (H_2O_2 + magnetite = ■). PAHs contents are based on the measurements by GC–MS. Experimental conditions were: solid matrix = 2 g, volume of solution = 20 mL. Oxidant dose was used according to H_2O_2:Fe molar ratio of 20:1.
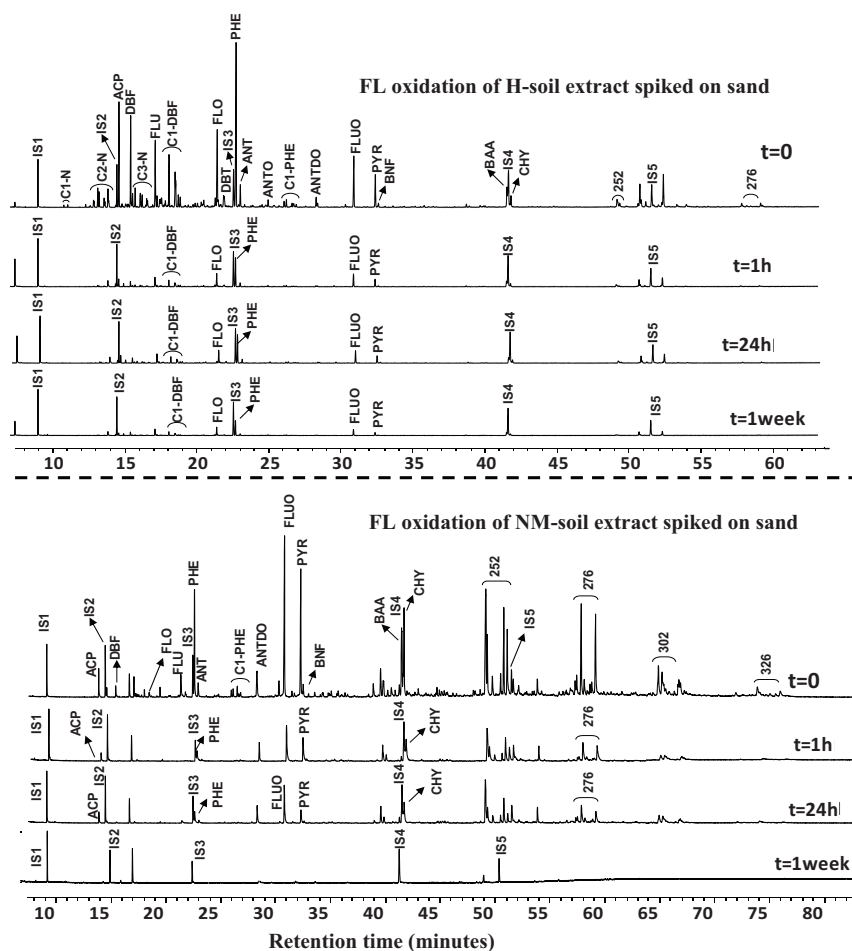
Fig. 4. Molecular distribution obtained by GC–MS of H and NM organic extract (spiked on sand) before oxidation ($t = 0$) and after different oxidation times by FL oxidation (H_2O_2 + magnetite). The compounds are detailed in Table S1. Experimental conditions were: solid matrix = 2 g, volume of solution = 20 mL. Oxidant dose was used according to H_2O_2:Fe molar ratio of 20:1.

$t = 0$ was ∼4 mg g^{-1} corresponding to the initially added amount of fluorenone. It means that no carbon was condensed in sand and ultimately no effect of matrix (quartz sand) was observed. Fluorenone degradation is represented by C_t/C_0 versus oxidation time (Fig. 1) where C_t is the concentration at specific time point and C_0 is the concentration at $t = 0$ (∼3975 μg/g) determined by GC–MS. Blank experiments (conducted with magnetite alone, without oxidant) revealed negligible degradation (<3%) of fluorenone. When magnetite was the catalyst, almost 90% of fluorenone abatement was achieved within 48 h, and after 1 week of oxidation fluorenone was completely removed. On the contrary, slight decrease (15–20%) was obtained when H_2O_2 was catalyzed by soluble Fe^{II}. The same degradation yield was observed for H_2O_2 without iron activation, thereby underscoring the inability of soluble Fe^{II} to act as catalyst at circumneutral pH.

3.2. Oxidation of two PAHs contaminated soils

Oxidative degradation of PAHs from H and NM soils was investigated by the same treatments including HP, F and FL. A very slight decrease in pH was observed (from 8.35 to 8.10 in H and from 7.20 to 7.10 in NM) after the introduction of reactants and then stayed almost constant throughout experiment. The soil samples of concern showed slightly higher concentration of total PAHs in H soil (∼1369 μg/g) than in NM soil (∼1279 μg/g). The ratio of low molecular weight PAH (LMW: sum of naphthalene to pyrene concentrations) over high molecular weight PAH (HMW: sum of

benzo[a]anthracene to benzo[g,h,i]perylene concentrations) was calculated for each experimental time. LMW/HMW for $t = 0$ suggests the predominance of LMW-PAHs in H soil with a value of 5.36 whereas NM soils is characterized by a higher proportion of HMW-PAHs (0.96). The achieved results exhibit negligible PAHs removal at circumneutral pH whatever the used catalyst (magnetite or soluble Fe^{II}). Increasing of oxidant dose did not improve the PAHs degradation (Fig. S2). This absence of degradation can be caused by several factors related to soil nature and pollution type. These factors may include unavailability of PAHs to oxidation, soil matrix effect or high reactivity of H_2O_2 and •OH radical with soil constituents. To understand this lack of degradation, we firstly isolated organic extract from soil matrix to improve the PAH availability before starting oxidation reaction.

3.3. PAHs degradation in organic extracts spiked on sand

Both H and NM soils were extracted via the procedures given in Section 2.2. The corresponding organic extracts isolated from soil were homogeneously spread on sand and dried followed by their oxidation through HP, F and FL treatments. The oxidant dose was used according to H_2O_2:Fe molar ratio of 20:1 and the pH was 6.8 ± 0.2. The PAHs quantified by GC–MS represented in terms of C_t/C_0 against time are shown in Fig. 2. Negligible degradation was observed for blank experiments. After 1 week of oxidation in the FL system, almost 90% and 95% of 16 PAHs degradation was achieved in H (i.e. remaining concentration of 16 PAHs: ∼125 μg/g) and NM
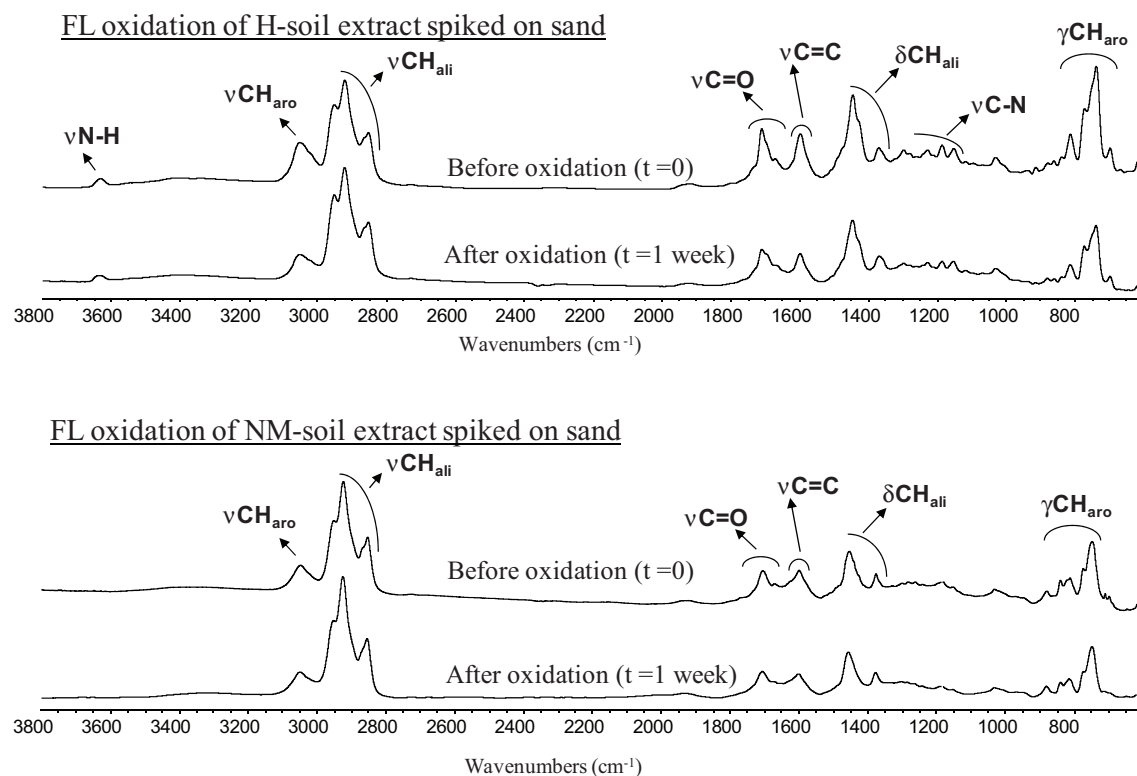
Fig. 5. FTIR spectra of (a) organic extract from H soil and (b) organic extract from NM soil before ($t = 0$) and after oxidation (1 week) by FL oxidation (H_2O_2 + magnetite). Organic extracts from H and NM soil were added to sand and after evaporation of the solvent, oxidation was performed. Experimental conditions were: solid matrix = 2 g, volume of solution = 20 mL. Oxidant dose was used according to H_2O_2:Fe molar ratio of 20:1.

extract (i.e. remaining concentration of 16 PAHs: ~76 µg/g), respectively. A colorimetric test showed that H_2O_2 was still present in the first four points (from 1 h to 48 h) and disappeared after 1 week in the FL system. Only 10–15% of degradation was achieved when soluble Fe^{II} was used as catalyst. The same degradation efficiency was found for H_2O_2 alone without iron activation.

To observe the degradation selectivity, the behavior of individual 16 PAHs was studied (Fig. 3). Before oxidation ($t = 0$), the total PAHs contents in both H and NM extract–sand mixture were almost the same as in real soil. FL oxidation did not show any preferential degradation for LMW or HMW PAHs (Fig. 3). No selective degradation was observed for both soils although the PAHs composition was different in both soils with varying proportions of LMW and HMW-PAHs. These results are in agreement with those obtained with abiotic air oxidation process at 100 °C during 180 days which showed a non-selective PAHs degradation [20]. However, thermal desorption treatments that consists of exposing the soil to high temperature (650 °C) operated in both H and NM soil samples showed selective PAHs degradation with less efficiency towards HMW-PAHs [16]. The non-selective degradation way observed here could be explained by the probable production of surfactants which would render HMW-PAHs available in the aqueous phase and ultimately degradable by radical hydroxyl [21,22]. The surfactants can be produced as a result of partial oxidation of hydrocarbons and/or native organics having surfactant-like properties. These surfactants accompanying the Fenton oxidation of hydrocarbons in soil are eventually removed by further chemical oxidation and/or biodegradation [21,22]. In addition formation of reductants (e.g. superoxide) could act as surfactant and contribute in enhanced desorption of PAHs [23].

A problem that may arise during PAHs oxidation is the risk of incomplete degradation (mineralization) and the consequent production of degradation by-products. In this study, the identity of

the oxidation by-products was determined by GC–MS (Fig. 4) and µFTIR (Fig. 5). The GC–MS molecular analysis of the PAHs distribution in organic extracts of H and NM showed clearly the absence of new reaction products (Fig. 4). Molecular distributions are almost the same at different oxidation time points as compared to $t = 0$ for both H and NM extracts suggesting a non-selective degradation.

The findings by µFTIR revealed that the initial EOM characteristics remained unchanged after FL oxidation for both H and NM organic extract (Fig. 5). The stability of the relative intensity of oxygenated bands (especially νOH: 3700–3100 cm^{-1} and νC=O: 1745–1705 cm^{-1}) suggests the absence of oxygenated by-products formation. Moreover, the similarity of aliphatic profiles (νCH_{ali}: 3000–2800 cm^{-1} and δCH_{ali}: 1470–1360 cm^{-1}) and aromatic profiles (νCH_{aro}: 3100–3000 cm^{-1}, νC=C: 1620–1590 cm^{-1} and γCH_{aro}: 900–700 cm^{-1}) reveals that no major molecular reorganization occurred (Fig. 5). These findings are in agreement with µFTIR and suggest the absence of degradation products by FL oxidation in EOM-sand system and a non-selective degradation.

All these results reveal that PAH removal can be achieved when the organic extracts were subjected to oxidation away from the soil matrix. Another interesting point of these results is the strong reactivity of magnetite to catalyze oxidation for PAHs degradation compared to ferrous salt. But its reactivity was observed only when oxidation was operated for PAHs in EOM spiked on sand after its separation from the soil matrix. Once PAH availability was increased by their extraction from soil, oxidation lead to their degradation. This highlights the important role of the PAHs availability in the determination of treatment efficiency in a contaminated soil whatever the catalyst used.

Various soil factors like soil organic matter (SOM) and mineral composition could contribute to hinder PAHs degradation [4,24–26]. In general, an increase in SOM will reduce the Fenton oxidation efficiency through scavenging of •OH radicals and increasing

of PAHs retention [4,25]. It was stated that the PAH degradation extent was inversely proportional to the total organic carbon (TOC) for the soil with TOC above 5% [24]. In our soil samples, TOC in both soils is close to 10% and 7% for H and NM, respectively (Table 1). Contents of 16-PAHs (1369 and 1279 μg/g for H and NM, respectively) represent less than 2% of soil TOC and EOM (36 and 13 mg g^{-1} for H and NM, respectively) corresponds to almost 36% and 17% of H and N soil, respectively, of the TOC of tested soils. Rest of the organic matter was trapped in soil as IOM. This suggests that SOM competition and retention capacity can largely affect oxidation efficiency. In addition to SOM, clay particles contribute to the strong sorption of PAHs in soils [27]. As a matter of fact, PAHs on sandy soil are degraded easier than PAHs adsorbed on organic rich soils or clay rich soils [26]. Even if, in our case, H and NM soils are dominated by sand mineral fractions (more than 60%), clay and fine silt (~25%) can induce an efficiency limitation.

Therefore, in addition to the PAH availability, radical scavenging particles such as SOM, fine soil fractions and carbonates could inhibit or limit the degradation extent. This was examined in the following section by increasing the PAHs availability and then oxidizing the organic extract in the presence of soil.

3.4. PAHs degradation in pretreated soils

In this section, the same extraction procedures as in Section 3.3 were used but without separation of EOM from solid (mineral + IOM). In other words, soil was agitated in chloroform for 45 min at 60 °C that was allowed to evaporate before oxidation. The purpose was to increase the PAHs availability, but by keeping the soil matrix. Then, as in previous sections, H_2O_2 oxidation with or without iron catalyst was performed with H_2O_2:Fe molar ratio of 20:1. The observed pH values were 8 ± 0.2 in H and 7 ± 0.2 in NM and stayed almost constant throughout experiment. The concentration of 16-PAH is represented in terms of C_t/C_0 versus time in Fig. 6. No oxidation was observed in blank experiments. Very small degradation (<5%) was obtained without or with soluble Fe^{II} activation in HP and F treatments. However, a degradation extent of 50–60% was achieved after 1 week of oxidation for both soils when magnetite was used as catalyst. After 1 week, remaining concentration of 16 PAHs by FL treatment was ~678 μg/g and ~594 μg/g in H and NM soils, respectively. Here PAHs degradation was significantly improved as compared to soil oxidation without any pretreatment (Section 3.2), but reduced as compared to oxidation of organic extract spiked on sand (Section 3.3). Therefore, soil matrix effectively contributes to the decrease in the degradation extent (from 90% to 55%). This reduction in degradation extent in soil could be exerted by a natural oxidant demand (NOD) resulting in additional nonproductive oxidant depletion [28]. Such natural materials can include IOM inherited probably from coal, coke, as well as reactive mineral materials including metal-based oxides and carbonates. Higher IOM was observed in both soils from almost 60% and 80% of TOC, respectively, for H and NM soils which could cause this lower degradation extent. These scavenging soil constituents compete for oxidant radicals with organic contaminants and thus lowering their degradation in soil as compared to organic extracts spiked on sand. Carbonate contents in H soil were 10 times higher than NM soil, but a slight difference in term of degradation efficiency between soils was observed. Thus the impact of carbonate content on PAH removal is not significant in our systems. In conclusion, both soil matrix (IOM and mineral fractions) and PAHs availability were responsible of the lack of PAHs degradation in soils.

Similar to the oxidation of organic extract in sand, GC–MS and μFTIR analyses revealed the absence of by-products in soils (data not shown). Also the PAHs degradation was non-selective in both soils. Results also highlight the importance of catalyst used as
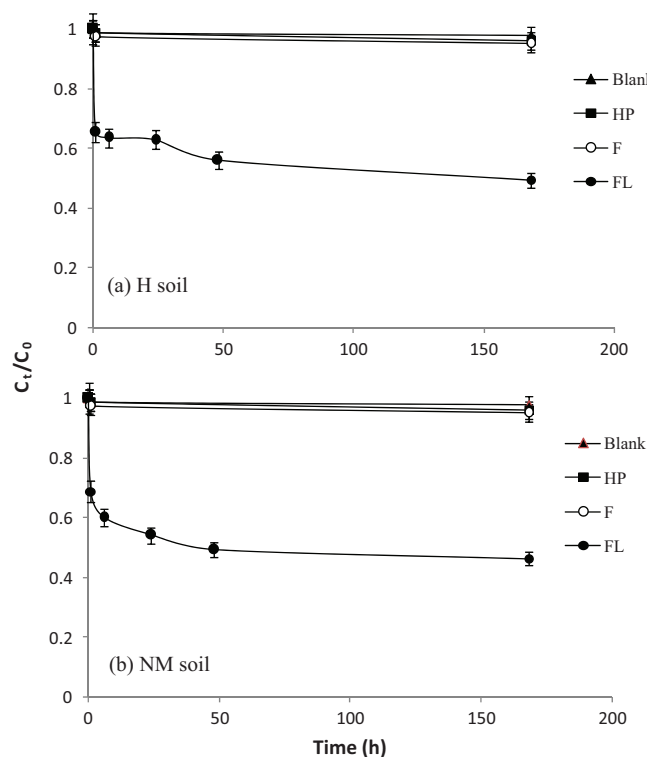

Fig. 6. PAHs degradation in organic extracts in the presence of soils (H and NM) during oxidation experiments by: H_2O_2 alone without iron activation (■ – HP), H_2O_2 + soluble Fe^{II} (○ – F) and H_2O_2 + magnetite (● – FL). Blank (▲) experiment was performed in the presence of magnetite but without any oxidant. Soils were subjected to an extraction pretreatment but without isolation of organic extract and after evaporation of solvent, oxidation was performed. This degradation is represented in terms of C_t/C_0 where C_t is the sum concentration of 16 PAHs at specified oxidation time and C_0 is the sum concentration at $t = 0$ (before oxidation) measured by GC–MS. Lines are only visual guide. Experimental conditions were: solid matrix = 2 g, volume of solution = 20 mL. Oxidant dose was used according to H_2O_2:Fe molar ratio of 20:1.

magnetite was able to catalyze Fenton oxidation at circumneutral pH. Interestingly, degradation efficiency was almost the same in both cases either with or without soluble Fe^{II}. The rapid oxidation of Fe^{II} and/or the complexation of ferrous ion with soil constituents at circumneutral pH could explain this inability of Fe^{II} to catalyze the H_2O_2 decomposition.

Pretreatments using ethanol or cyclodextrin (CD) as solubility-enhancement agents (or availability-enhancement agents) were also used to increase in situ the PAHs availability in both soils, and to evaluate the impact of enhancing PAHs availability on oxidation yield. In the magnetite catalyzed Fenton-like oxidation system, ethanol has slightly higher degradation efficiency (20%) than that of cyclodextrin (15%) after 1 week of reaction time. No significant degradation was, however, noted in the absence of catalyst or in the presence of soluble Fe^{II}. A similar low degradation efficiency (~20%) was previously obtained for ethanol-Fenton treatment of PAHs contaminated soil compared to Fenton alone [29]. This limited-degradation extent may be due to (i) the low capacity of ethanol or CD to enhance the PAH availability, and/or (ii) the scavenging effect. In fact, CD can consume a significant amount of oxidant species that would otherwise be available to degrade contaminants, as previously reported in aqueous solution [30]. So, injection of enhancement solubility agents may increase the oxidant demand of the system. However, the scavenging effect concerns only CD, as ethanol was evaporated from reactor before oxidation.

4. Conclusions

This study represents the following important points for ex situ and in situ chemical oxidation of contaminated soils:

(1) Higher efficiency of magnetite to catalyze chemical oxidation at circumneutral pH was the main finding of this study. The use of magnetite as iron source for Fenton oxidation was appeared as a promising and innovative way for chemical oxidation of PAHs. As Fe^{II} was found unable to catalyze the H_2O_2 decomposition at circumneutral pH, injection of magnetite particles in contaminated soils could be especially advantageous for in situ remediation of contaminated matrices where pH cannot be adjusted. This approach provides a cost effective solution for soil remediation without pH adjustment contrary to other known methods where more than one reagent is used (e.g. iron + chelating agents). In addition, magnetite, non-toxic mineral, is structurally and catalytically stable and can be used for further oxidation cycles.

(2) Both PAHs availability and soil matrix seem to be the most influencing parameters in ISCO technologies. Improvement of PAHs availability can be correlated with the enhancement of PAHs oxidation in soil samples. Contents of mineral and organic constituents in soil can affect the oxidation mechanism and degradation efficiency. Before designing an oxidation experiment, evaluation of PAH availability as well as characterization of soil constituents should be carefully carried out. Finally, reactivity of magnetite for application would be more prominent in contaminated soil without such limitations of PAHs availability or significant matrix effect.

These findings regarding the ability of magnetite, the most stable mixed-valence oxide, to promote oxidation in soils have important practical implications for chemical oxidation technologies.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2012.01.007.

References

[1] ITRC, Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, second ed., ITRC, ISCO Team, Washington, DC, 2005.
[2] E. Ferrarese, G. Andreottola, I.A. Oprea, Journal of Hazardous Materials 152 (2008) 128–139.
[3] R.J. Watts, P.C. Stanton, J. Howsawkeng, A.L. Teel, Water Research 36 (2002) 4283–4292.
[4] V. Flotron, C. Delteil, Y. Padellec, V. Camel, Chemosphere 59 (2005) 1427–1437.
[5] S.R. Kanel, B. Neppolian, H. Choi, J.W. Yang, Soil and Sediment Contamination 12 (2003) 101–117.
[6] H.J.H. Fenton, Journal of the Chemical Society Transactions 65 (1894) 899–910.
[7] J. Sahl, J. Munakata-Marr, Remediation Journal 16 (2006) 57–70.
[8] C. Sirguey, P. Tereza de Souza e Silva, C. Schwartz, M.-O. Simonnot, Chemosphere 72 (2008) 282–289.
[9] X. Xue, K. Hanna, C. Despas, F. Wu, N. Deng, Journal of Molecular Catalysis A: Chemical 311 (2009) 29–35.
[10] S.-S. Lin, M.D. Gurol, Environmental Science and Technology 32 (1998) 1417–1423.
[11] S.H. Kong, R.J. Watts, J.H. Choi, Chemosphere 37 (1998) 1473–1482.
[12] S.R. Kanel, B. Neppolian, H. Jung, H. Choi, Environmental Engineering Science 21 (2004) 741–751.
[13] R. Matta, K. Hanna, S. Chiron, Science of the Total Environment 385 (2007) 242–251.
[14] K. Hanna, T. Kone, G. Medjahdi, Catalysis Communications 9 (2008) 955–959.
[15] X. Xue, K. Hanna, M. Abdelmoula, N. Deng, Applied Catalysis B: Environmental 89 (2009) 432–440.
[16] C. Biache, L. Mansuy-Huault, P. Faure, C. Munier-Lamy, C. Leyval, Environmental Pollution 156 (2008) 671–677.
[17] P. Faure, P. Landais, L. Griffault, Fuel 78 (1999) 1515–1525.
[18] O. Ruau, P. Landais, J.L. Gardette, Fuel 76 (1997) 645–653.
[19] K. Benhabib, P. Faure, M. Sardin, M.-O. Simonnot, Fuel 89 (2010) 352–359.
[20] C. Biache, T. Ghislain, P. Faure, L. Mansuy-Huault, Journal of Hazardous Materials 188 (2011) 221–230.
[21] J. Gryzenia, D. Cassidy, D. Hampton, Chemosphere 77 (2009) 540–545.
[22] A.C. Ndjou'ou, D. Cassidy, Chemosphere 65 (2006) 1610–1615.
[23] R.J. Watts, B.C. Bottenberg, T.F. Hess, M.D. Jensen, A.L. Teel, Environmental Science and Technology 33 (1999) 3432–3437.
[24] B.W. Bogan, V. Trbovic, Journal of Hazardous Materials 100 (2003) 285–300.
[25] S. Jonsson, Y. Persson, S. Frankki, B. van Bavel, S. Lundstedt, P. Haglund, M. Tysklind, Journal of Hazardous Materials 149 (2007) 86–96.
[26] A. Goi, M. Trapido, Environmental Technology 25 (2004) 155–164.
[27] F.K. Kawahara, B. Davila, S.R. Al-Abed, S.J. Vesper, J.C. Ireland, S. Rock, Chemosphere 31 (1995) 4131–4142.
[28] J.S. Haselow, R.L. Siegrist, M. Crimi, T. Jarosch, Remediation Journal 13 (2003) 5–16.
[29] S. Lundstedt, Y. Persson, L. Öberg, Chemosphere 65 (2006) 1288–1294.
[30] K. Hanna, S. Chiron, M.A. Oturan, Water Research 39 (2005) 2763–2773.